

23 July 73
(DATE)

MEMORANDUM FOR THE RECORD

SUBJECT: Opinion Request -

More Chemical Catalysts

Attached is self-explanatory material from the Department of State.
May we have your opinion by 3 Aug 73.

Please state degree of interest and whether we will receive requirements.

25X1A

(IMAGE)

COMMENTS:

Comments will be welcome. Please let me know whether or not to expect any. Thanks.

DISTRIBUTION:

OSI: *ok*
OER: *— defer OSI*
AF: *✓ — no obj*
NAVY: *✓ — no comments*
ARMY: *✓*
DIA: *✓*
GSD: *✓*

*Raz Pardon told
17 Aug 73
✓ earlier*

State, USAF declassification & release instructions on file

E2 IMPDET
CL BY: 007622

Gov-C

Chemical Catalysts



DEPARTMENT OF STATE

Washington, D.C. 20520

BUREAU OF INTERNATIONAL SCIENTIFIC
AND TECHNOLOGICAL AFFAIRS

STATINTL

July 6, 1973

MEMORANDUM

TO: EUR/SES - Mr. Raymond Pardon

FROM: SCI/SA - Royal J. Wald *RJW*

SUBJECT: Report on Joint US-USSR Meeting on
Chemical Catalysis Project

Attached are 2 copies of the Report and Record,
(with transmittal memo from Halpern to Baldeschwieler),
concerning last month's meeting in Moscow of the
chemical catalysis project group in the field of
coordination complexes and organometallic compounds.

Attachment:

As stated.

Nomi

7/9/73

Attached for comment is the working group report on sub topic # 1
of the Chemical Catalysis cooperative field entitled
Catalysis by Coordination Complexes and Organometallic Compounds.

Annexed to the Record of Proceedings is the proposed program
for joint research.

Any comments or suggestions would be appreciated.

Ray Pardon

CHICAGO • ILLINOIS 60637

DEPARTMENT OF CHEMISTRY
KENT CHEMICAL LABORATORY • GEORGE HERBERT JONES LABORATORY
SHARLE CHEMICAL LABORATORY

July 2, 1973

To: John D. Baldeschwieler
From: Jack Halpern
Re: U.S.-U.S.S.R. Joint Program on Catalysis by Coordination Complexes
and Organometallic Compounds

Attached are the official English and Russian versions of the Report of the Meeting pertaining to the above program that was recently held in Moscow. The American participants in this meeting were J. P. Collman (Stanford), G. W. Parshall (du Pont), J. F. Roth (Monsanto) and myself.

I consider the principal accomplishments of this meeting to be the following:

1. Several days of very intensive scientific discussions in the course of which a considerable amount of scientific information was exchanged and the appreciation on the part of the participants on each side of the research activities of their counterparts was greatly enhanced.

2. The agreement on three specific topics of cooperative research for priority implementation and the designation of a principal investigator from each side for each of these topics. From the standpoint of scientific content the program is thus all set to go and I feel that we have reason to be pleased by the selection of participants from the Soviet side.

Agreement was also reached in principle on two other important matters although the details of these remain to be resolved, namely (1) a visit by the three Soviet principal investigators (Shilov, Vol'pin and Ermakov) to the U. S. A., probably in October or November of this year, and (2) the exchange of junior scientists between the participating Soviet and American laboratories. I am disappointed that we could not agree on the immediate implementation of this exchange but apparently our Soviet colleagues still have some matters to resolve in this connection and the best that we could achieve was agreement that the arrangements for such implementation would be completed by the end of 1973.

Details of these and a number of other matters are elaborated in the appended report.

Memorandum to John D. Baldeschwieler

Page 2

July 2, 1973

favorably impressed by the high quality of Soviet science in the field of this particular program and also by the splendid hospitality that was extended to us. We shall be hard pressed to match the latter when our Soviet colleagues visit us.

lr

enclosures: (English and Russian Report)

cc: ✓ Dr. N. P. Neureiter } (enclosures: English & Russian Report)
Dr. J. Tech }

Dr. M. K. Wilson
Dr. T. W. DeWitt
Dr. J. P. Collman } (enclosure: English report)
Dr. E. L. Muettertides }
Dr. G. W. Parshall }
Dr. J. F. Roth }

To the Co-Chairmen of the U.S.-U.S.S.R. Working Group
on Cooperation in the Field of Chemical Catalysis

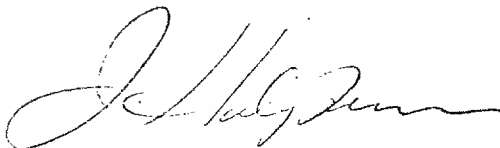
June 27, 1973

REPORT

The US and USSR Coordinators of the Joint Program on Catalysis by Coordination Complexes and Organometallic Compounds (Theme I) herewith transmit to the Co-Chairmen of the U.S.-U.S.S.R. Working Group on Cooperation in the Field of Chemical Catalysis the Record of its meeting, signed in Moscow June 27, 1973.

The Record, which is attached, describes the proceedings of the meeting of participants in the Joint Program that was held in Moscow June 18-22, 1973 and lists the topics and projects approved and recommended for the implementation of the Program.

The Program Coordinators recommend approval of the proposed priority projects so that cooperative work may begin at an early date.



U.S. Coordinator

(J. Halpern)



U.S.S.R. Coordinator

(A. Shilov)

RECORD OF PROCEEDINGS

of the U.S.-U.S.S.R. Meeting on Theme I

"Catalysis by Coordination Complexes and Organometallic Compounds"

Moscow, 27 June 1973

The U.S.-U.S.S.R. meeting on Theme I "Catalysis by Coordination Complexes and Organometallic Compounds" was held in Moscow June 18-22, 1973.

The U.S. side was represented by the coordinator of Theme I, Professor J. Halpern (University of Chicago), Professor J. Collman (Stanford University), Dr. G. Parshall (du Pont Company), and Dr. J. Roth (Monsanto Company). The Soviet side was represented by the coordinator of Theme I, Professor A. E. Shilov (Institute of Chemical Physics -I.C.P.), Academician B. A. Dolgoplosk, (Institute of Petro-Chemical Synthesis -I.P.-C.S.), Academician N. N. Semenov (I.C.P.), Professor E. A. Blumberg (I.C.P.), Professor Yu. I. Ermakov (Institute of Catalysis), Dr. V. M. Frolov (I.P.-C.S.), Dr. A. B. Gagarina (I.C.P.), Dr. O. N. Jakubovitch (Physical-Chemistry Institute -P.-C.I.), Professor V. B. Kazanski (Institute of Organic Chemistry), Professor M. L. Khidekel (I.C.P.), Professor G. I. Likhtenshtein (I.C.P.), Professor Z. K. Maizus (I.C.P.), Dr. Yu. D. Novikov (I.C.P.), Dr. Yu. A. Shvetsov (I.C.P.), Dr. I. P. Skibida (I.C.P.), Professor E. I. Tinjakova (I.P.-C.S.), Professor M. E. Volpin (Institute of Organo-Element Compounds), Dr. K. I. Matveev (Institute of Catalysis).

-2-

The following subjects were discussed at the Meeting:

1. Investigations of the mechanisms of activation of C-H and C-C bonds in organic compounds by transition metal complexes;
2. Investigations of molecular nitrogen complexes and the mechanisms and products of nitrogen fixation;
3. Catalytic properties of surface complexes;
4. Complexes of CO and CO₂ and their reactions;
5. Catalytic hydrogenation;
6. Role of the nature of ligands in catalytic complexes in oxidation reactions;
7. Catalysis in hydrocarbons oxidation;
8. Catalytic reactions of π -allyl complexes.

During the period of the meeting the American scientists had the opportunity to visit several laboratories of the Institute of Chemical Physics and the Institute of Organo-Element Compounds. These visits led to a considerably greater appreciation of the scale and the level of Soviet investigations in the field of catalysis.

During the period of the meeting the American scientists gave the following lectures which took place in the Institute of Chemical Physics, the Institute of Organo-Element Compounds and the Institute of Organic Chemistry.

-3-

Professor J. Halpern -

"Mechanisms of oxidative addition reactions;"

"Oxidation of CO and olefins in the presence of
transition metal complexes."

Professor J. Collman -

"Supported organometallic and coordination catalysts" and

"Reactions of sodium tetracarbonyl ferrate (-II)."

Dr. G. Parshall -

"Catalytic activation of aromatic compounds."

Dr. J. Roth -

"Carbonylation of alcohols" and

"Asymmetric catalytic hydrogenation."

The large number of Soviet scientists who were present at the lectures were able to enlarge their knowledge of American catalytic investigations considerably.

In accordance with the previously agreed upon program for Theme I, the meeting has adopted a plan of joint research (see Appendix). As a result of the discussion of the reports presented from the groups of laboratories headed by Academician N. M. Emanuel (I.C.P.), from the laboratory of Academician B. A. Dolgoplosk (I.P.C.S.), and from the laboratories of Prof. A.R. Gantmakher (P.C.I.) and Prof. V. B. Kazanski (I.O.C.), the meeting considers it desirable to enlarge the future joint program on Theme I to include from the Soviet side the research on catalysis which is performed by the above laboratories.

-4-

To fulfill the joint research program the meeting recommends that in October-November 1973 three Soviet senior scientists should visit several US centers which are active in the investigation of catalysis by coordination complexes and organometallic compounds.

To participate in the joint research, three American and three Soviet junior scientists should be sent to work for six months in the laboratories of the other country on the basis of equivalent exchange. The program of this exchange is to be completed by the coordinators by the end of 1973.

The meeting recommends to the cooperating sides consideration of the possibility of simultaneous publication in the USA and in the USSR in English and in Russian, respectively, a book on catalysis containing contributions from American and Soviet scientists. The two coordinators will present a plan for the book by 1 July 1974.

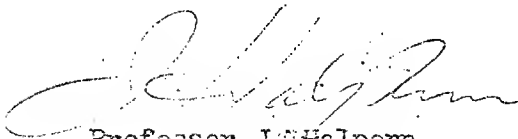
The meeting recommends that a regular Seminar should be organized for discussions of the scientific results and the future investigations encompassed by the joint research program on Theme I. It is considered desirable that this Seminar should be held at least once every two years with the location alternating between the two countries.

-5-

To increase the familiarity of American and Soviet scientists with research on coordination catalysis in the other country, the meeting considers it desirable to encourage scientists of each countries to publish results of their research in the journals of the other country.

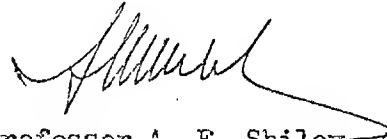
Coordinators of Theme I

"Catalysis by Coordination Complexes and Organometallic Compounds"



Professor J. Halpern

USA



Professor A. E. Shilov

USSR

Appendix

PROPOSED PROGRAM FOR JOINT RESEARCH ON THEME I

"Catalysis by Coordination Complexes and Organometallic Compounds"

I. Activation of small molecules (N_2 , O_2 , CO , CO_2).

Investigation of activation mechanisms and the products of reactions.

Principal Investigators

from the US

from the USSR

J. Halpern

M. E. Volpin

A. For priority implementation:

1. Investigation of organic synthetic reactions involving CO and CO_2 .

2. Investigation of the oxidation of organometallic compounds including vitamin B_{12} and its analogs.

B. For future implementation:

1. Investigation of the reduction of molecular nitrogen, including models of biological nitrogen fixation.

Suggested Participants

from the US

from the USSR

Dr. Bulen

A. E. Shilov

2. Investigation of the role of oxygen complexes of transition metals in oxidation reactions.

Suggested Participants

from the US

from the USSR

J. Halpern, J. Collman

N.M. Emanuel, A.E. Shilov

-2-

II. Investigation of mechanisms of activation of C-H and C-C bonds in organic compounds by metal ions and complexes.

Principal Investigators

from the US

from the USSR

E. Muetterties

A. E. Shilov

A. For priority implementation:

1. Investigation of the kinetics and mechanism of (i) halogenation of C-H bonds in the presence of Pt(II) and Pt(IV) complexes and (ii) exchange of ethylene with D₂O catalyzed by Pt(II) complexes.

2. Investigation of the mechanisms of activation and the reactions of saturated hydrocarbons in solutions containing platinum metal complexes.

III. Investigation of the interaction of organometallic and coordination compounds with supports and the catalytic properties of the resulting complexes.

Principal Investigators

from the US

from the USSR

J. Collman

Yu. I. Ermakov

A. For priority implementation:

1. Investigation of the interactions of organometallic compounds of group VI and VIII metals with various functional groups on the surface of oxide supports.

2. Investigation of the composition and reactivity of the resulting surface organometallic compounds.

-3-

3. Investigation of the catalytic properties of the resulting surface compounds in hydrogenation, oxidation, and disproportionation reactions.

IV. Investigation of the role of ligands in coordination catalysis and the mechanisms of hydrocarbon oxidation.

Principal Investigators

from the US

from the USSR

J. Halpern

I.V. Kalechitz, K. I. Matveev

A. For priority implementation:

None

B. For future implementation:

1. Investigation of the mechanisms and the regulation by ligands of the catalytic activity of complexes in reactions of olefin oxidation to carbonyl compounds.

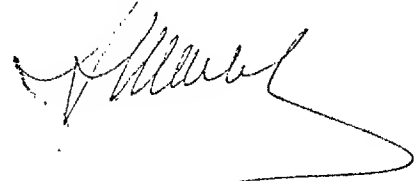
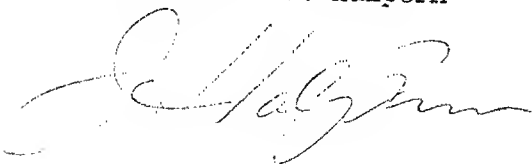
Coordinators of Theme I

for the USA

for the USSR

Professor J. Halpern

Professor A. E. Shilov



7/10/73

NOMI

- Subject: 1) US Working Group on Chemical Catalysis
Sub-Topic # 3
In-Depth Study of Selected Catalytic
Systems- An Exchange of Correspondence
on work priorities;
- 2) Preliminary Evaluation of US-USSR
Symposium on Scientific &
Technical Information ;

For your information and any comment.

Ray Pardon

Gulf Research & Development Company

T. R. Hopkins
PRESIDENT
Ulrich Merten
DIRECTOR
PROCESS SCIENCES DEPARTMENT

P. O. Drawer 2038
Pittsburgh, PA 15230

July 6, 1973

Professor O. V. Krylov
Institute of Chemical Physics
Academy of Sciences, USSR
Vorobjevskoye Shaussee, 2-B
Moscow, 117334, USSR

Dear Oleg Valentinovich:

Your letter of May 15, 1973 arrived here on June 17. The next step is to make final arrangements for our visit to the USSR. I propose that we start immediately on this because I feel strongly that the sooner this can be done, the better.

We will need an agenda, giving the time and place of the planning meeting and which institutions in the USSR we will visit, if any. After I receive this information, we will need nearly a month to obtain the necessary visas, etc. Also, we must ask you to obtain the necessary hotel reservations for us, as this information must be included on the agenda.

I suppose that by now you must have received my letter of May 7, but I am enclosing a copy in case you have not. In this letter I have identified those principal investigators who are planning to come to the USSR, and I have given you my thoughts concerning the meeting. Is this plan generally acceptable to you; if not, how do you wish to proceed?

I think that we can plan to spend a week or ten days in the USSR, depending upon the requirements of the agenda. Besides the planning meeting, the cooperation could be initiated by visits to one or more of the laboratories which may be involved in the program; it would be particularly helpful if the U.S. principal investigators had the opportunity to meet and talk with some of those Soviet Post-Doctoral scholars who may be coming to the U.S. as part of this program, if they have been identified. Since we will be the visitors, we will, of course, try to adapt our plans to your convenience. Therefore, please send me a tentative agenda as soon as possible, and I will make the arrangements here.



DATE 7/6/73

FROM W. Keith Hall

TO O. V. Krylov

SHEET NO. 2

I have studied your maximal plan for Subject III. First of all let me say that all of the elements look very attractive. This makes it difficult to assign priorities; more information is really needed concerning the specific objectives of the different principal investigators. Presumably this will be available at the planning conference in the USSR. However, three rules may be applied:

- (a) Work in the USSR should compliment work in the US, and vice versa; each principal investigator should have his counterpart in the other country.
- (b) The work, insofar as possible, should lead to standardization of methods and cross-comparison of results; also, insofar as possible, work in both countries should be carried out on the same catalysts.
- (c) Lower priority will be assigned to research of a supporting nature than to the preparation and characterization of catalysts for the banks, and mechanism studies on these materials, unless this work is coupled in some way with direct catalytic measurements. Chemisorption, chemical physics and various spectroscopic measurements may be expected to make important contributions to the program, but only if the results can be directly related to the catalyst systems being studied intensively.

With these thoughts in mind, I make the following appraisal in response to your question concerning which subjects from your maximal plan should be given priority in 1973. Perhaps, after more discussion, other options may be found better. The final choice, of course, is yours.



DATE 7/6/73

FROM W. Keith Hall

TO O. V. Krylov

SHEET NO. 3

- (1) Catalytic Oxidation
 - (a) Preparation and Characterization of Molybdate Catalysts - Boreskov
 - (b) Transition Metal and Non-transition Metal Molybdates - Krylov et al
 - (c) Dehydrogenation Over Ferrite Spinel - Bujanov
 - (d) Investigation of Short-Lived Surface Complexes - Kazanski
- (2) Hydrogenation on Pure Metals and Alloys
 - (a) Hydrogenation over Group VIII Metals and Their Alloys - Gelbstein
 - (b) Hydrogenation of Dienes, Etc., Over Membranes of Pd and Pd-Ni - Smirnov and Griaznov
- (3) Acid-Base Catalysis
 - (a) Isomerization of Butenes - Topchieva
 - (b) NMR Study of Interaction of 1-Butene With Acid-Base Centers - Kazanski
 - (c) Quantum - Chemical Calculations - Zhidomirov
 - (d) Decationated Zeolites - Model Reactions - Topchieva

With kindest personal regards, I am

Sincerely yours,



W. Keith Hall

Attachment

P.S. Please address your reply to my new address, viz.:
Department of Chemistry
University of Wisconsin-Milwaukee
Milwaukee, Wisconsin 53201

cc: John D. Baldeschwieler
Thomas DeWitt
George Keulks
John Turkevich
Richard Kokes
Michel Boudart
W. Keith Hall



Gulf Research & Development Company

T. R. Hopkins
Ulrich Merten
Pittsburgh, PA 15230

P. O. Drawer 2033
Pittsburgh, PA 15230

May 7, 1973

Professor O. V. Krylov
Institute of Chemical Physics
Academy of Sciences, USSR
Vorobjevskoye Shaussee, 2-1
Moscow, 117334, USSR

Dear Oleg Valentinovich:

Since I have not yet received a reply to my letter to you dated January 30, 1973, I fear that either my letter or your reply has been lost in the mails. Therefore, I am sending you a copy herewith. Moreover, I am informed that our correspondence may be accelerated if you reply via Dr. Aykejian.

Let me up-date you on the situation here. Since the Joint Commission has given its approval of our general program, we are moving ahead with plans to get some catalysts prepared and characterized for this work. Money to carry out the work has not yet been made available, but I have been assured that this will be forthcoming in the immediate future.

We plan to make and characterize some catalysts for the in-depth study in the three fields: catalytic hydrogenation over metals, catalytic oxidation over oxides, and acid catalysis. These preparations will be mostly selected from those on which we have mutually agreed would be worthwhile. Half of each useful preparation will be sent to each catalyst bank. We hope that you will follow a similar procedure. This procedure may lead to some duplication of catalysts made in the two countries, but I believe that this will be valuable because it will enable us to cross compare results at an early stage in the cooperation.

In the area of hydrogenation, Professor John Turkovich of Princeton University will concentrate on the problems of making small metal particles (10 Å to 50 Å) of uniform size and on mounting them on supports. Initially, work will concentrate on Pt, Pd and Pd-Ag alloys; small metal clusters of

5/7/73

W. Keith Hall

O. V. Krylov

2

Pt-Au are also being considered. It is my understanding that John Turkevich will write you in the near future inviting you to nominate a Soviet Post Doctoral student to work with him on this project.

In the area of catalytic oxidation, Professor George Keulks of the University of Wisconsin-Milwaukee will undertake the preparation and characterization of several molybdate and several ferrite catalysts along the lines described in my letter of January 30. Some of the acid catalysts will also be made at Milwaukee; I shall personally direct this work. Initially, we will aim at some model systems: alumina mounted on silica and alumina in silica (to draw on the background provided by Pitkethly et al, J. Phys. Chem., 74, 2197 (1970); *ibid*, 75, 220 (1971); silica-supported germania to exploit some very interesting work of M. J. D. Low which is now in press (J. Colloid and Interface Sci.) and a series of oxide catalysts varying from very basic to very acidic (MgO to zeolites) as outlined in my earlier letter. As time goes on I would like also to obtain some large pore zeolites in which Ge has been substituted for Si and Ga for Al. I am now sure that this can be done, but there are some serious obstacles in making homogeneous pure preparations. Would you like to suggest Soviet Scientists to participate in these programs? Fairly fluent English will be helpful here; John Turkevich is the only one among us who speaks Russian.

Beyond these immediate objectives, of course we all have some well-defined ideas concerning experiments which should be done, and I am sure you and your collaborators have also. To promote real collaboration, however, it would be best to follow your suggestion and have a small meeting to work out the details. Perhaps this should be followed by another about six months later. Preferably, the one in the summer would be held in the USSR and in the USA in the winter. Several of my colleagues have noted that the International Conference on Molecular Sieves meets in Zurich September 3-7 and have suggested the week preceding or that following as a convenient time for a meeting in Moscow. Does this seem reasonable to you? What are your wishes?

As presently conceived the US delegation will include: Professors J. Turkevich, G. W. Keulks, R. J. Kokes, M. Boudart, myself, and possibly J. D. Baldeschwieler. Presumably you will have a like number. May I suggest that each member be given 30 minutes to outline to the others his views on what the vital problems are in his area. This will consume one day. Then, suppose we break into three working groups (one for each area) for more detailed discussion and to draft written reports outlining the work to be done and by whom. I suppose that this may take several days. At a preset time, however, we might then reconvene into plenary session for a final discussion and amendment of what we have written. I am advancing these suggestions with the thought that it is good to have all of the participants return home with the same set of notes.

I am sure the US participants will want to visit one or more laboratories of their Soviet colleagues if this is possible and if time permits.

With kindest personal regards, I am

CONFIDENTIAL

USAF POSITION ON COMMUNIST BLOC VISITORS

Visitors: US-USSR Chemical Catalysis Project

Project and Sponsor:

LGZ	AFSC	FTD	OTHER
N/O		N/O	

8. USAF also provides the following:

Opinion # 59-1 Due 3 Aug 73

Passed to IIAGE 2 Aug 73

Classified by: CIA/IIAGE
EXEMPTED FROM GENERAL
DECLASSIFICATION SCHEDULE
ON FILE WITH DATE 11/5/52
EXEMPTION CATEGORY 2
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